COATINGS

CHANGES IN NANOSIZE COATINGS BY SULFURIC ACID SOLUTIONS

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The interaction of a nanosize coating with HCl solutions proceeds in two stages. I. Swelling of the coating is accompanied by an increase of its index of refraction as a result of the air present in the pores in the film being replaced by the more strongly refracting solution and washing of the more weakly refracting oxides, penetrating from the glass substrate, out of the coating. II. Dissolution of the coating is accompanied by a decrease of its thickness and index of refraction. The overall result is expressed as an increase or decrease of these indicators depending on which of the indicated processes predominates.

Key words: sol-gel technology, nanosize coating, composite, index of refraction and thickness of nanosize coating, etching in acid solutions.

Composites consisting of a substrate of colorless sheet float-glass coated with a functional nanosize film are widely used for fenestration in modern construction and architecture [1, 2].

The main requirement for any material coming into contact with the ambient environment is to remain functional over a long period of time. For light and sun screening composites the main characteristics are optical — the light transmission and reflection coefficients. The fine dust, moisture and active gases present in air affect nanosize coatings, changing the composite's properties – dust has an abrasive effect and degrades the state of the surface; moisture and active gases partially dissolve a nanosize layer or leach individual components out of it, changing unpredictably the composition, index of refraction and reflection coefficient of the composite.

The objective of the present work is to determine the changes produced in the refractive index of composites with nanosize coatings by hydrochloric acid solutions.

Large-size glass ($1100 \times 2000 \times 4$ mm) coated with a high-reflectivity multicomponent sol-gel film was used for these studies [3]. Samples with dimension $50 \times 50 \times 4$ mm were cut from the glass. They were kept at room temperature in water solutions of hydrochloric acid with different normal concentration ranging from 0.01 to 0.5 N. The duration of the interaction was varied from 1 to 60 min. The index of re-

fraction n and thickness h of the films before etching (n_{ini}, h_{ini}), after etching (n_{etch}, h_{etch}) and after etching followed by firing at temperature 450°C ($n_{etch.f}$, $h_{etch.f}$) were measured with an LÉF ZM 1 ellipsometer.

The low firing temperature of the composite, which is required to secure the nanosize coating and remove from it moisture, residues of the solvent and decomposition of the initial components used to prepare film-forming solutions, is limited by the temperature at which the glass substrate starts to deform and is probably too low for all components to melt and interact with a full-fledged inorganic polymer — a glassy coating — being formed.

This is confirmed by results obtained in [4], where the dependence of the melting temperature on the size of the aluminum powder particles is calculated theoretically and confirmed in practice. Aluminum with 5 nm particles melts at 880 K; reducing the particle size to 1.6 nm lowers the temperature to 780 K, which is 50 – 150 K lower than the tabulated value 933 K [5].

The melting temperature of the filming-forming composition used in this work cannot be predicted because there are no data on the equilibrium diagram of the three-component system Bi_2O_3–Fe_2O_3–TiO_2. Since the melting temperatures of the initial oxides are 2143 K (TiO_2), 1838 K (Fe_2O_3) and 1098 K (Bi_2O_3) and the maximum transverse size of the cord-shaped pseudo-dipolar particles in the coating is 50 nm, it is doubtful that full-fledged melting and interaction of all components will occur at firing temperature 723 K. For this reason it can be conjectured that the coating comprises a

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TABLE 1. Index of Refraction and Thickness of Nanosize Coatings Treated with HCl Solutions with Different Concentrations C and Treatment Times τ

HCl		Refractive index of coating[*]								
C, N	τ, min	n_{ini}	n_{etch}	Δn_1	$\Delta n_1 / n_{ini}$, %	$n_{etch.f}$	Δn_2	$\Delta n_2 / n_{ini}$, %	Δn_3	$\Delta n_3 / n_{ini}$, %
0.01	1	1.97	2.04	0.07	3.66	2.07	0.10	4.98	0.03	1.32
0.01	30	2.00	2.03	0.03	1.73	2.10	0.10	5.03	0.07	3.31
0.01	60	2.00	2.06	0.06	0.97	2.03	0.03	1.52	0.03	1.50
0.05	1	1.99	2.04	0.05	2.69	2.08	0.09	4.54	0.04	1.85
0.05	30	1.96	1.99	0.03	1.77	2.08	0.12	5.96	0.08	4.19
0.05	60	1.95	1.99	0.05	2.42	1.99	0.04	2.04	−0.01	−0.38
0.1	1	1.96	2.00	0.04	2.16	2.12	0.17	8.48	0.12	6.32
0.1	30	1.95	2.04	0.10	4.97	2.07	0.12	6.18	0.02	1.22
0.1	60	1.98	1.98	0.001	0.07	2.00	0.02	1.26	0.02	1.19
0.1	1	2.02	2.07	0.05	2.69	2.11	0.10	4.83	0.04	2.13
0.1	30	2.06	2.00	−0.06	−2.77	2.03	−0.03	−1.45	0.03	1.32
0.1	60	2.01	1.94	−0.07	−3.37	1.89	−0.12	−5.91	−0.05	−2.53

Coating thickness,[**] Å								
h_{ini}	h_{etch}	Δh_1	$\Delta h_1 / h_{ini}$, %	$h_{etch.f}$	Δh_2	$\Delta h_2 / h_{ini}$, %	Δh_3	$\Delta h_3 / h_{ini}$, %
495	493	−2	−1	404	91	18	89	18
459	462	3	1	362	97	21	100	22
492	522	30	6	461	31	6	61	12
477	494	17	4	405	71	15	88	19
437	487	50	12	374	63	14	114	26
454	464	10	2	399	55	12	65	14
414	447	33	8	319	95	23	128	31
486	425	−61	−13	371	115	24	54	11
485	449	−36	−7	368	118	24	82	17
362	394	32	9	287	76	21	108	30
395	283	−112	−28	284	111	28	−1	−0.3
463	268	−195	−42	270	193	42	−2	−0.4

[*] $\Delta n_1 = n_{etch} - n_{ini}$; $\Delta n_2 = n_{etch.f} - n_{ini}$; $\Delta n_3 = n_{etch.f} - n_{etch}$;

[**] $\Delta h_1 = h_{etch} - h_{ini}$; $\Delta h_2 = h_{ini} - h_{etch.f}$; $\Delta h_3 = h_{etch} - h_{etch.f}$.

xerogel with a definite glassy phase fraction and residual porosity.

The interaction of a nanosize coating with a corrosive liquid medium is comprised of two competing phenomena. Swelling occurring when liquid penetrates into the pores of the xerogel is accompanied by displacement of the more weakly refracting air and an increase of the refractive index of the coating in accordance with the expression [6]

$$n_{eff} = n_1 - Po(n_1 - n_3) - (n_2 - n_3) f(P/P_0), \qquad (1)$$

where n_1, n_2 and n_3 are the refractive indices of the layer material, adsorbed water and air, respectively; $f(P/P_0)$ is the adsorption isotherm expressed in general form; and, Po is the porosity.

The increase of the refractive index can also be due to low-refracting sodium oxide, penetrating from the glass sub-

strate during deposition and subsequent firing of the nanosize film, being washed out of the coating. This is supported by the observation of sodium oxide in hydrochloric acid solutions after the samples have been etched.

The thickness of the layer after interaction (etching) increases at the same time. In the chemistry of high-molecular compounds, any increase of the thickness of the sample is estimated by the degree of swelling

$$\alpha = \frac{m - m_0}{m_0}, \qquad (2)$$

where m_0 and m are the mass of the initial and swollen polymer, respectively.

The swelling can be limited, when α reaches a constant magnitude, or unlimited, when α passes through a maxi-
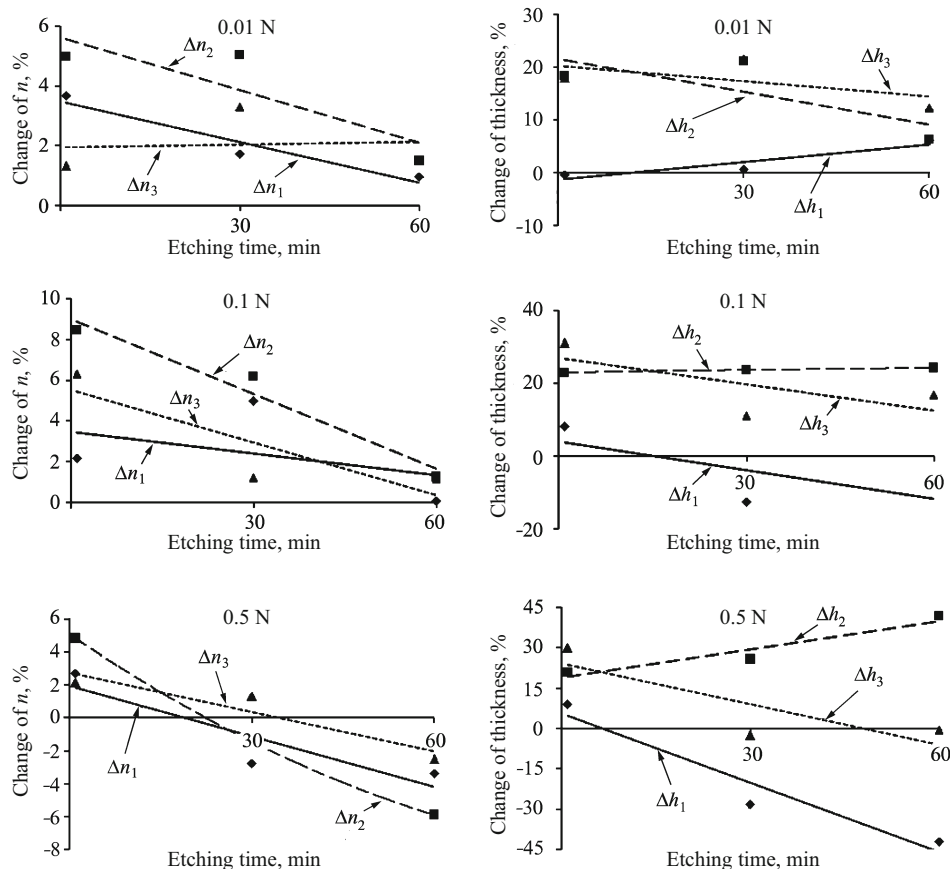
Fig. 1. Change of the refractive index n and thickness h of nanosize coatings as a function of the etching time. The hydrochloric acid solution concentration is indicated on the plots.

mum, after which the polymer dissolves. In this case the swelling is the initial stage of dissolution [7].

The second stage of the interaction, which is superposed on the swelling, is dissolution of the coating. The thickness decreases evenly. The refractive index also decreases because the low-refracting oxides penetrating from the substrate increase in the residual nanosize coating layer. Theoretical calculations (neglecting the porosity of the nanosize coating and the oxides which have penetrated from the substrate very likely being washed out) show that such a thickness change can decrease n by almost 5% (from 2.43 to 2.31).

To determine the true change of the thickness and refractive index of the nanosize layer any effect due to swelling must be ruled out. For this, the etched samples were subjected to repeated firing.

Since the effects due to swelling and dissolution are superposed on one another as a result of the interaction of a nanosize layer with the acid solution, the overall result can be expressed as an increase or decrease of the thickness or index of refraction depending on which of these two processes dominates in a concrete etching regime.

To determine the combined effect of swelling and dissolution on the characteristics of a nanosize coating the relative (with respect to the initial values) changes of the refractive index $\Delta n_1 = n_{etch} - n_{ini}$ and thickness $\Delta h_1 = h_{etch} - h_{ini}$ of the

films after treatment in hydrochloric acid were calculated. The values of $\Delta n_2 = n_{etch.f} - n_{ini}$ and $\Delta h_2 = h_{ini} - h_{etch.f}$ make it possible to judge the change of the indices as a result of the dissolution of the coatings. Finally, the quantities $\Delta n_3 = n_{etch.f} - n_{etch}$ and $\Delta h_3 = h_{etch} - h_{etch.f}$ make it possible to determine quantitatively the effect due to swelling and the effect of swelling on the refractive index.

Analysis of the experimental results (see Table 1 and Figs. 1 and 2) shows that as the concentration of the hydrochloric acid solution and the duration of the action of the acid on the samples increase the values of the Δh_1 and Δn_1 decrease systematically. The differential Δh_1 increases only when the concentration of the etching solution is low and the interaction is brief. In this case, probably, a nanosize coating swells without dissolving appreciably.

The change of the refractive index of the film resulting from the dissolution of the coating, estimated by the value of Δn_2, decreases with increasing acid solution concentration and increasing etch time.

The dissolution rate of the coating, expressed as the increase in Δh_2, increases at the same time. The effect of a 0.01 N solution is an exception: prolongation of etching slows down dissolution and decreases Δh_2.

The effect of swelling Δh_3 becomes weaker with increasing solution concentration and interaction time because the
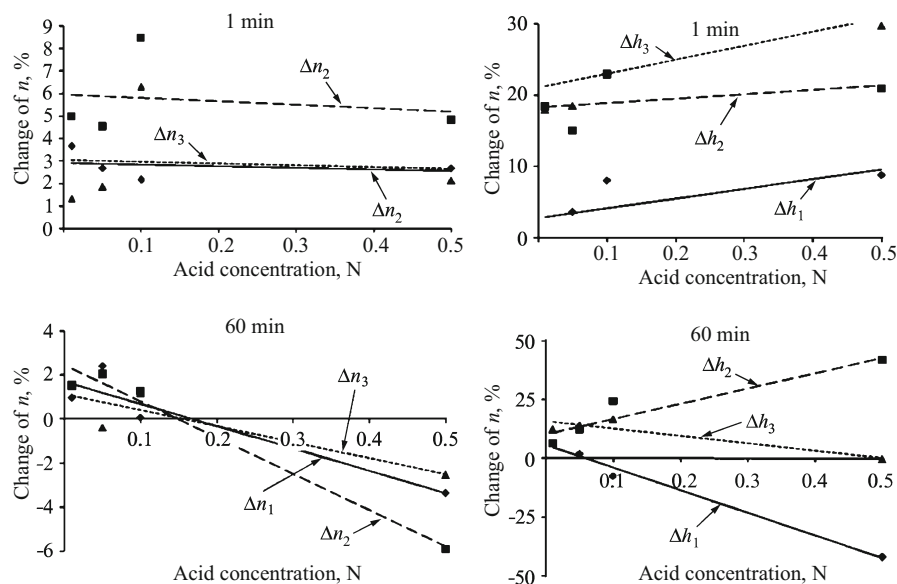
Fig. 2. Change of the refractive index and thickness of nanosize coating as a function of the acid solution concentration. The etching time (in min) is indicated in the plots.
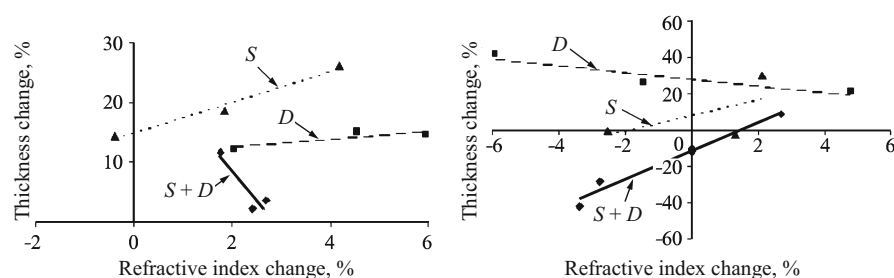

Fig. 3. Interrelation of refractive index and thickness changes at different stages of the interaction of nanosize coatings with an acid solution. The normal acid concentration is indicated on each plot. The changes of the parameters at each stage are: S) swelling; $S + D$) swelling + dissolution (after the films are etched); D) dissolution (after etching with subsequent firing).

dissolution of the nanosize coating intensifies. When samples are held for a short time 1 min the increase of the swelling is proportional to the solution concentration. Probably, the dissolution processes cannot develop over such a short period of time.

The value of Δn_3 decreases as the concentration of the etching solution and the interaction time increase. Only an increase of the holding time at 0.01 N has virtually no effect on the change in this parameter.

The results of the studies are summarized in Fig. 3.

The thickness increment resulting from swelling is always accompanied by an increase of n of nanosize coatings because of pores being filled by a high-refracting (compared with air) acid solution.

The interrelation of thickness and refractive index changes at the swelling + dissolution stage is in direct (0.05 N solution plots in Fig. 3) or inverse (0.05 N solution plots) proportion depending on whether swelling (holding in a 0.05 N solution) or dissolution (holding in a 0.05 N solution) dominates in a concrete process. It should be noted that no swelling is observed after the samples were held in a 0.05 N acid solution for 30 and 60 min; the thickness of a nanosize coating immediately after etching is less than the initial value.

The thickness dependence of the refractive index at the dissolution stage is in direct or inverse proportion. Swelling intensifies the washing of low-refraction oxides, migrating from the substrate, out of the body of the nanosize coating, and if the dissolution of the film is negligible, the refractive index of the residual layer will increase, as observed in the case of holding in a 0.05 N solution. In the absence of or very small swelling (etching in a 0.05 N solution) there is virtually no washing out, and after dissolution the material of the residual layer of the nanosize coating becomes enriched with the low-refraction component of the substrate, the enrichment being all the greater, the more intense the dissolution.

In summary, the interaction of a nanosize coating with a liquid aggressive medium is comprised of two opposing stages. The swelling due to the penetration of the liquid into the pores in xerogel is accompanied by an increase of the thickness of the nanosize coating and at the same time the acid solution replaces low-refraction air in the pores in the body of the film. In addition, an increase of the refractive index could be due to low-refraction oxides, penetrating from the glass substrate during deposition of a nanosize film, being washed out of the coating material.

The second stage of the interaction is dissolution of the coating. In this process the thickness decreases in a regular manner. The refractive index decreases because of the in-

crease in the residual layer of the nanosize coating of low-refraction oxides of the glass substrate.

The overall results can be expressed as in increase or decrease of the thickness and index of refraction depending on which process dominates in a concrete etching regime.

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